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# DETERMINATION OF TOTAL ACIDITY BY THE BARITE METHOD: CONDITIONS OF APPLICABILITY FOR THE ANALYSIS OF HUMIC ACIDS

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**Abstract.** The dependence of the results of total acidity determinations of humic acids (HA) by the barite method on the quantitative $Ba(OH)_2$/HA ratio has been shown. For a strongly acidic preparation of peat HA, an optimum ratio was found: 65 mequiv of barium hydroxide per gram of HA. It was established that when this proportion is used, the results of the analysis do not depend on HA concentration in solution. It is concluded that the determination conditions found here are applicable to any HA preparations. However, when maximum values of total acidity are obtained, it is recommended that control analysis be carried out at higher excess $Ba(OH)_2$ concentrations.

**Key words:** *humic acids, total acidity, determination, effect of reagent excess.*

## Introduction

Humic acids are the products of natural microbiological synthesis and form the main part of organic substances in water and soil media. Because of their specific chemical structure (they are high molecular weight aromatic polyoxypolycarboxylic acids) HA readily interact with metal ions. However, the quantitative description of this process is a very complex problem [1—4]. The reason for this is the polyelectrolyte nature of HA excluding the application of classical approaches to the study of complexation in the HA-metal system, which are based on the derivation of stoichiometric equations of the reactions. One of the must widespread indirect methods for evaluating the ability of HA to interact with metals is the determination of their total acidity which means the total number of exchange protons per unit mass of HA [1,5,7,8].

This characteristic is not universal, and its value depends on the experimental method of determination [9,10] because different proportions of acidic protons in the polyelectrolyte take part in the reaction depending on kinetic or thermodynamic factors. In spite of this, there are indications in the literature that the values of total HA acidity obtained by different methods are similar [1,9]. Direct potentiometric titration in an aqueous medium is generally used for the determination of acid groups content. Nevertheless, the use of this simple method for the analysis of HA acidity involves the following difficulties. HA titration curves do not contain distinct inflection points and their processing requires the plotting of statistical models.

The use of different models leads to different results [1,8,9,11]. The application of potentiometric titration in non aqueous media can improve curve quality only slightly [1,5]. The authors of ref. [9] have successfully used calorimetric titration which makes it possible to obtain curves with the only inflection point corresponding to total acidity.

However, the instrumentation for this method is relatively complex, which prevents its wide application. Methods for the determination of total acidity from the increase in methoxy groups content after methylation with diazomethane have also been described [1,5]. This procedure is evidently very laborious and cannot be widely used.

Hence, the above methods of total acidity determination are complicated as regard either instrumentation or the processing of results. Therefore, most authors prefer the barite method [5,6,10,13] which is based on back titration of excess barium hydroxide remaining in solution after the removal of humic acids in the form of an almost insoluble residue of barium humate. In this case the titration curve of HA, the interpretation of which is difficult, is replaced by the titration curve of a strong base,

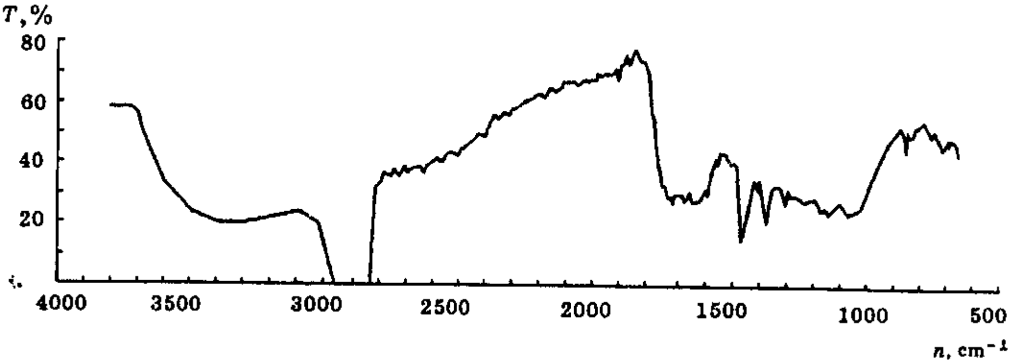

Fig. 1. Typical IR spectrum of isolated preparations of peat humic acids.

$Ba(OH)_2$. This procedure is very simples and, therefore, very widespread.

The artifacts of this procedure are usually mentioned: possible excessive values of the results and their scattering because of $CO_2$ absorption [1] and incomplete precipitation of barium fulvates when unfractionated preparations are used [14]. Moreover, none of the often cited papers dealing with the application of the barite method to the determination of HA total acidity [1,5,6] present any grounds for the choice of quantitative $Ba(OH)_2$/HA ratios used. Thus, in the most widespread method proposed in 1965 by Schnitzer and Gupta [6], it is recommended that 40—80 mequiv $Ba(OH)_2$ per gram of HA be taken for analysis. The present investigation was undertaken in order to determine the significant this factor: the quantitative reagent/HA ratio for the determination of total acidity by the barite method.

## Experimental

HA preparations used for determinations were a sum of humic and fulvic acids isolated by alcaline extraction from eight peats of different origins and geobotanic compositions with the acid of a modified procedure [15]. In order to preserve the water-soluble HA fraction, the initial stage of peat treatment with not water was emitted. Powdered peat was treated with a benzene-ethanol mixture (1:1), dried at 40–60°C, and extracted with 0.1 M NaOH. The alcaline extract was demineralized by passing through the H-form of KU-2-8 cation exchanger (pH of solutions obtained by this procedure was 2.95–3.4). HA content in the eluate was determined gravimetrically by evaporating of a precise aliquot quantity of the solution. For elemental analysis and IR spectroscopy, solid preparations were obtained by evaporation of demineralized HA solutions on a rotor evaporator followed by drying in a dissicutor over $P_2O_5$ to constant weight. Elemental composition of HA preparations is given in Table 1. Their typical IR spectrum is shown in Fig. 1.

For HA isolation 0.1 M NaOH was obtained by dissolving dry alkali (pure for analysis) in distilled water.

For titrations 0.2 M $Ba(OH)_2$ solution was prepared by dissolving a BaO feed in distilled water with subsequent storage for two or three days for carbonate precipitation. In order to prepare the working solution, the initial solution was powered from the precipitate, filtered through a paper filter (blue band) and diluted with distilled water (without carbonate) to the required concentration.

Carbonateless water was prepared by boiling distilled water for one hour. It was stored in a vessel supplied with a calcium chloride tube with asearite.

Back titration was carried out by using 0.0999 M HCl "for volume determinations" ("Baker Analysed" Reagent).

Potentiometric titration was performed with the aid of a pH-340 device with standard glass and calomel electrodes.

The all investigations of the effect of the concentration ratio $Ba(OH)_2$/HA on the results of total acidity determination were carried out by using an HA 7 preparation (Tables 1 and 2)

Table 1

Elemental composition of HA samples

| Sample | C | H | N | O | Ash content |
|---|---|---|---|---|---|
| 1 | 39.6 | 5.0 | 2.0 | 51.0 | 11.1 |
| 2 | 48.8 | 5.0 | 2.4 | 43.7 | 1.9 |
| 3 | 49.4 | 4.9 | 2.3 | 43.4 | 3.0 |
| 4 | 50.2 | 4.8 | 1.1 | 43.9 | 3.3 |
| 5 | 50.2 | 4.9 | 1.9 | 43.0 | 4.1 |
| 6 | 49.7 | 5.0 | 2.1 | 43.2 | 1.6 |
| 7 | 50.1 | 4.8 | 2.1 | 43.0 | 1.4 |
| 8 | 50.7 | 4.7 | 2.5 | 42.1 | 2.1 |

Table 2

| Sample | HA concentration in solution, mg·ml$^{-1}$ | Total acidity, mequiv·g$^{-1}$ Ba(OH)$_2$/HA = const | Total acidity*, mequiv·g$^{-1}$ Ba(OH)$_2$/HA = var |
|---|---|---|---|
| 1 | 1.4 ± 0.1 | 10.7 ± 1.0 | 8.4 ± 1.0 |
| 2 | 2.2 ± 0.2 | 13.0 ± 1.5 | 6.0 ± 0.8 |
| 3 | 0.5 ± 0.1 | 7.4 ± 1.2 | 7.5 ± 1.0 |
| 4 | 0.7 ± 0.1 | 8.0 ± 2.0 | 7.6 ± 1.5 |
| 5 | 1.2 ± 0.1 | 7.0 ± 1.0 | 6.0 ± 1.5 |
| 6 | 0.8 ± 0.1 | 8.7 ± 1.1 | 9.3 ± 1.0 |
| 7 | 2.1 ± 0.2 | 12.0 ± 0.6 | 7.6 ± 1.3 |
| 8 | 1.4 ± 0.1 | 8.5 ± 0.5 | 6.8 ± 0.6 |

* Values determined according to the procedure described in ref. [11].

**Procedure of total acidity determination.** An aliquot quantity of HA solution (5 ml) containing 1–10 mg of the solid substance was placed in a 25 ml glass vessel, air was buried out by bubbling the solution with argon, the calculated almost of the $Ba(OH)_2$ working solution was added, the vessel was sealed, shaken, and left to stand at room temperature for complete precipitation of barium humates and fulvates. The precipitate was filtered of on a glass filter (GF/F) and the vessel and the filter were ashed with three portions of carbonateless distilled water. The filtrate was combined with wash waters and titrated potentiometrically with 0.1 M HCl. A blank determination was carried out simultaneously for an aliquot quantity of carbonateless water into which the same amount of $Ba(OH)_2$ had been added. Total acidity was calculated according to ref. [5] from the equation.

$$TA = \frac{(V_0 - V_{HA})N}{m} ,$$

where TA is the total acidity, mequiv·g$^{-1}$; $V_0$ is the volume of HCl consumed for sample titration, ml; $N$ is the HCl concentration, mequiv·ml$^{-1}$; and $m$ is the mass of the HA solid substance in the aliquot quantity, g.

## Result and discussion

Two sets of experiments were carried out to investigate the effect of $Ba(OH)_2$/HA quantitative ratios on the results of HA total acidity determination by the barite method: a) at a constant HA concentration the excess amount of $Ba(OH)_2$ introduced was varied, b) excess reagent amount was constant and HA concentration was varied.

The aim of the first set of experiments was to estimate the effect of reversibility of barium humates and fulvates precipitation on the determination. For this purpose the aliquot amounts of HA solution at the same concentration were titrated by adding different quantities of $Ba(OH)_2$. Constant volumes of solutions being titrated were ensured by adding the required amount of carbonateless distilled water. Blank experiments with the same amount of the alkali were performed simultaneously. The results can be seen in Fig. 2.

This figure shows that when the quantity of $Ba(OH)_2$ used in the reaction ranges from 30 to 65 mequiv·g$^{-1}$ HA, the values of total acidity are profoundly affected by the excess amount of the reagent. Moreover, it is possible to determine reliably reproducible values of HA total acidity only after the concentration ratio of 65 mequiv of $Ba(OH)_2$ per gram of HA has been attained. The existence of this dependence is probably due to the reversibility of barium humates and fulvates precipitation.

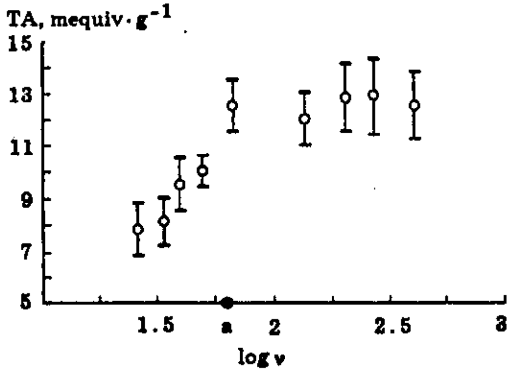

Fig. 2. Effect of excess $Ba(OH)_2$ on the determined value of total acidity (TA) 15 ml of HA solution at a concentration of 0.4 g·l$^{-1}$ + calculated quantity of 0.1 N $Ba(OH)_2$ + distilled water). $\nu$ is the mequiv of added $Ba(OH)_2$ per gram of HA; a corresponds to 65 mequiv·g$^{-1}$.

*Nuclide Release*. Coughtrey P.J., Bell J.N.B., Roberts T.M.(Eds.); Special publication № 3; British Ecological Society; Blackwell Scientific; Oxford, pp. 42–62.

4. Linnik P.N. and Nabivanets B.I. (1986) *Forms of Metals Migration in Fresh Surface Waters* Ed: Gidrometeoizdat,. Leningrad, 268 p. (in Russian)
5. Schnitzer M and Khan S.U. (1972) *Humic Substances in the Environment*. Marcel Decker, N.Y., pp. 37–54.
6. Schnitzer M. and Gupta U.C. (1965) Determination of acidity in soil organic matter. *Soil Sci. Soc. Amer. Proc.*, 29, 274–277.
7. Flaig W., Beutelspacher H. and Rietz E. (1975) In: *Soil Components*. Gieseking J.E.(Ed.), V.1, Springer-Verlag. Berlin, pp. 145–164.
8. Aiken G.R., McKnight D.M., Wershaw R.L. and MacCarthy P. (Eds.) (1985) *Humic Substances in Soil, Sediment and Water*. John Wiley & Sons. N.Y., 387 p.
9. Perdue E.M., Reuter J.N. and Chosal M. (1980) The operational nature of acidic functional group analyses and its impact on mathematical descriptions of acid-base equilibria in humic substances. *Geochim.Cosmochim.Acta*. 44, 1841–1851.
10. Piccolo A. and Camici L.(1990) A comparison of two methods for the determination of total acidity of humic substances. *Int.J.Environ.Anal.Chem.*, 41, 65–69.
11. Ephraim J.H., Boren H., Arsenie I., Pettersson C. and Allard B. (1989) A combination of acid-base titration and derivatization for functional group determination of an aquatic fulvic acid. *Sci.Total Environ*. 81/82, 615–624.
12. Brunelot J., Adrian P., Rouiller J., Guillet B. and Andreux F.(1989) Determination of dissociable acid groups of organic compounds extracted from soils, using automated potentiometric titration. *Chemosphere*, 19, Nos. 8/9, 1413–1419.
13. Gillam A.H. and Riley J.P. (1982) Microscale functional group analysis of marine and sedimentary humic substances. *Anal.Chim.Acta*. 141, 287–299.
14. Herbert B.E., Bortsch M. and Novak J.M.(1993) Pyrene sorption by water-soluble organic carbon. *Environ.Sci.Technol*. 27, 398–403.
15. Lowe L.E. (1992) Studies on the nature of sulfur in peat humic acids from Froser River delta, British Columbia. *Sci.Total Environ*. 113, 133–145.